Synopsis of the Thesis Entitled, "Materials for Hydrogen Generation, Storage, and Catalysis", to be submitted by Suresh Babu Kalidindi (S. R. No. 4-04-05-1-04065-0) Under the Supervision of Prof. Balaji R. Jagirdar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, for the PhD degree of the Institute Under the Faculty of Science.

Introduction

Hydrogen, nature's simple and the most abundant element has been in the limelight for the past few decades from the stand point of the so-called *hydrogen economy*. With a high calorific value (142 MJ/kg) that is three times as large as the liquid hydrocarbons, hydrogen has emerged as a promising and environmentally friendly source of energy for the future generations. However, on-board hydrogen storage is one of the bottlenecks for its widespread usage for mobile applications. Storing hydrogen in liquid or compressed form is extremely difficult because of its low density. One of the best alternatives is to store hydrogen in a chemical form. Despite extensive work in this area, none of the materials seem to satisfy the essential criteria of reversible hydrogen storage with high gravimetric content. With regard to chemical hydrogen storage, apart from metal hydrides, ammonia borane ($H_3N{\cdot}BH_3$, AB) is a promising prospect with a very high gravimetric storage of 19.6 wt% of hydrogen.

Objectives

1) Develop cost-effective and active first-row transition metal based catalysts for the generation of hydrogen from AB in protic solvents
2) Study the dehydrogenation of AB in fluorinated alcohols and acids in order to realize compounds that are suitable for regeneration.

3) Study the interaction of Cu^{2+} with AB in non-aqueous medium using ^{11}B NMR spectroscopy and powder XRD techniques.
4) Generation of highly pure hydrogen from ammonia borane in the solid state under mild conditions in the presence of late first row transition metal salts.
5) Synthesis of highly monodisperse ultrasmall colloidal Mg nanoparticles using the Solvated Metal Atom Dispersion (SMAD) method and digestive ripening technique; study the effect of size on the desorption temperature of MgH_2.
6) Synthesize Cu/ZnO and Cu/MgO nanocomposites from the individual metal nanoparticles using co-digestive ripening technique and establish the structure of the composites using TEM, EF-TEM, and powder XRD techniques.

Significant results

Hydrogen generation from AB in protic solvents was realized using first-row transition metal catalysts. Initial studies were carried out using Cu nanocatalyst synthesized by the solvated metal atom dispersion method (SMAD). The activity order was found to be Cu_2O > Cu@Cu_2O > Cu. In addition, the late first-row transition metal ions, Co^{2+}, Ni^{2+}, and Cu^{2+} ions were also found to be highly active towards AB hydrolysis. These ions assisted AB hydrolysis via in-situ formation of metal atoms/clusters. Cu^{2+} assisted the hydrolysis of AB via the in-situ generation of both H^+ and Cu clusters. At higher concentrations of AB, hydrolysis resulted in the evolution of NH_3 in addition to H_2 whereas, methanolysis afforded pure H_2. In the case of methanolysis, for catalyst/AB = 0.2, three equiv of H_2 were liberated in 2.5, 4.2, and 1.5 min when Co-Co_2B, Ni-Ni_3B, and Co-Ni-B nanopowders were used as catalysts, respectively.

Dehydrogenation of ammonia borane (AB) was carried out in 2,2,2-trifluoroethanol and trifluoroacetic acid in order to realize compounds that are suitable for regeneration. The final by-

product obtained after the catalytic dehydrogenation of AB in 2,2,2-trifluoroethanol was $NH_4^+B(OCH_2CF_3)_4^-$. The FTIR data showed that the B-O bond in $NH_4^+B(OCH_2CF_3)_4^-$ is slightly weaker compared to that in boric acid. Dehydrogenation of AB in trifluoroacetic acid in a controlled manner resulted in the formation of $[CF_3COO]^-[BH_2NH_3]^+$ as the final by-product. Ammonia-borane was regenerated from $[CF_3COO]^-[BH_2NH_3]^+$ by its reaction with $LiAlH_4$, which served as the hydride source.

Dehydrogenation of AB in non-aqueous medium and in the solid state were studied in hydrogen storage point of view. Cu^{2+} was found to activate the B–H bond in amine boranes in non-aqueous medium even at room temperature. As a result of the B–H bond cleavage in AB, $[H_3N{\cdot}BH_2]Cl$ species is formed. This compound reacts with unreacted AB via 3 separate pathways one involving hydrogen evolution, a second involving formation of a stable diammoniate of diborane cation $[(NH_3)_2BH_2]Cl$ without hydrogen evolution, and the third involving the formation of $[H_2NBH_2]_n$ and BNH_x polymers accompanied by the generation of H_2. Mechanisms of these pathways have been elaborated using ^{11}B NMR spectroscopy and powder X-ray diffraction methods. These studies demonstrate that Cu(II) salts can be used as effective initiators for the dehydrogenation of amine boranes.

Copper-induced hydrogen generation from AB in the solid state was also studied: for Cu^{2+}/AB = 0.05, two equiv of H_2 were liberated in 6.5 h at 333 K, which is equal to 9 wt% of the system. The ^{11}B MAS NMR studies showed that the reaction proceeds through the intermediacy of $[NH_4]^+[BCl_4]^-$ which eliminates the formation of borazine impurity, thereby affording pure H_2. The cost effectiveness of $CuCl_2$ makes this reaction scheme extremely attractive for real time applications.

In the context of hydrogen storage in metal hydrides, highly monodisperse colloidal Mg nanoparticles with a size regime of 2–4 nm were synthesized by using the SMAD method followed by digestive ripening technique. The Mg-HDA nanopowder was fully hydrided at 33 bar and 391 K. Onset of hydrogen desorption from MgH_2 nanoparticles was observed at a remarkably low temperature, 388 K compared to > 623 K in the case of bulk MgH_2. The present study is a step towards realizing hydrogen storage materials that could operate close to ambient conditions.

Colloids of Cu and Zn nanoparticles stabilized by 2-butanone have been prepared by the SMAD method. The as-prepared colloids which are polydisperse in nature have been transformed into highly monodisperse colloids by the digestive ripening process in the presence of hexadecylamine. Using this process, copper nanoparticles of 2.1 ± 0.3 nm and zinc nanoparticles of 3.91 ± 0.3 nm diameters have been obtained. Co-digestive ripening of Cu, Zn and Cu, Mg colloids resulted in the formation of Cu/ZnO and Cu/MgO nanocomposites, respectively. The structures of these nanocomposites were established using UV-visible spectroscopy, TEM, EF-TEM, and powder XRD techniques.